Electronic Supplementary Information

Rapid preparation of single-layer transition metal dichalcogenides nanosheets via ultrasonication enhanced lithium intercalation

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S1. Experimental Section

1. Chemicals

Three different transition metal dichalcogenides (TMDCs) compounds were used in powder form: MoS_2 (<2 µm, 99%, Sigma-Aldrich), WS_2 (<6 µm, 99.99%, Aladdin), and TiS_2 (<50 µm, 99.5%, Cerametek Materials). The n-butyllithium (n-BuLi, 2.4 M hexane solution) was purchased from Amethyst. All aqueous solutions in this study were prepared by using ultrapure water (Millipore, 18.2 M Ω).

2. Preparation of TMDCs NSs by ULI

In a typical reaction, MoS₂ powder (0.2 g, 1.25 mmol) was first added into a 25 mL Schlenk tube. Air in this tube was evacuated and then backfilled with pure Ar. After repeating the vacuum-Ar cycle for three times, the tube was sealed and protected with Ar. n-BuLi in hexane solution (1.04 mL, 2.50 mmol) was introduced into the Schlenk tube by a syringe. Ultrasonication enhanced lithium intercalation of MoS₂ was performed in a ultrasonic cleaner (53 kHz, 180W, SK3310HP, KUDOS) for different times (*Caution: It is strongly recommended that the rubber plug of the Schlenk tube should be tightly sealed by Parafilm in order to avoid the overflow of n-BuLi and keep safe*). Before exfoliation of the Li-intercalated MoS₂, the Schlenk tube was left to stand for 30 min and the residual n-BuLi in supernatant was removed. Under Ar flow, deaerated ultrapure water (10 mL) was carefully introduced into the tube drop by drop to avoid violent H₂ evolution.

The aqueous suspension of $MoS_2 NSs$ was sonicated for 30 min to complete the exfoliation (as for TiS₂, the tube should be immersed in iced water). Equal volume of ethanol was added into the $MoS_2 NSs$ suspension and centrifuged at 12000 rpm for 20 min. The precipitate was dispersed in ethanol and repeated the centrifugation procedure. Then, the sediment was separated and dispersed in ultrapure water. After centrifuged at 5000 rpm for 30 min, the large aggregates of MoS_2 in the bottom of the tube were discarded. The supernatant was collected and centrifuged at 12000 rpm for 1 h. The black sediment was dispersed in ultrapure water and the centrifugation was repeated for another two times. At last, the precipitate was dispersed in water and stored at 4 °C.

The preparation of WS_2 and TiS_2 NSs used similar procedures, except that the molar ratios of n-BuLi to TMDCs were 60:1 and 10:1 for WS_2 and TiS_2 , respectively.

3. Preparation of MoS₂ NSs by CLI

The reaction conditions and purification procedures for CLI method is the same to that of ULI, except that during the lithium intercalation step by n-BuLi no ultrasonication was used.

S2. Characterization

TEM images were taken on HT7700 (Hitachi, Japan) with acceleration voltage of 100 kV. HRTEM and SAED were performed on JEM-2100F (JEOL, Japan) with acceleration voltage of 200 kV. X-ray diffraction patterns were obtained by using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Cu K α radiation (λ =1.54178 Å). Atomic force microscopy (AFM) characterization was performed on Bruker Nanoscope IIIa. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 VersaProbe with Al K α (hv = 1486.6 eV) as the excitation source. The UV-Vis absorption spectra were recorded on a UV-Vis-NIR spectrophotometer (UV- 3600, Shimadzu, Japan). MoS_2 concentration was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 5300DV, Perkin Elmer) according to the reported procedure¹.



S3. TEM image of MoS₂ NSs and HRTEM image for folded edges

Fig. S1 (a) TEM image of MoS_2 NSs prepared by ULI for 3 h. (b) HRTEM image for folded edges of single-layer MoS_2 NSs prepared by ULI for 3 h.



S4. XPS spectra of MoS2 NSs

Fig. S2 (a) XPS spectra of Mo 3d and (b) S 2p core level peak regions of MoS_2 NSs prepared by ULI.

S5. Yields of MoS2 NSs at different molar ratios of n-BuLi to MoS2



Fig. S3 Yield of MoS₂ NSs obtained at different molar ratios of n-BuLi to MoS₂ by ULI method for 1h.



S6. TEM images of MoS2 powder sonicated at different times

Fig. S4 TEM images of MoS_2 powder under ultrasonication with different times in hexane. From a to d, the ultrasonication time is 0 h, 1 h, 2 h, and 3 h, respectively. The ultrasonication condition is identical to the ULI method, except without n-BuLi. The scale bar is 10 μ m.



Fig. S5 The average size of MoS_2 powder after different ultrasonication times for 0 h, 1 h, 2 h, and 3 h. Size statistics is based on more than 150 MoS_2 particles.





Fig. S6 UV-Vis absorption spectra of WS_2 (a) and TiS_2 (b) NSs prepared by ULI method. The insets show the photos of WS_2 (a) and TiS_2 (b) NSs aqueous dispersions in a sample bottle.

As shown in Fig. S6a, the excitonic peaks of bulk WS_2 located at about 520 nm and 640 nm have almost vanished, which is a sign of formation of single-layer $1T-WS_2$ NSs and suggests successful exfoliation of WS_2^2 . Absorption peak near 600 nm in Fig. S6b is similar to the reported value of TiS_2 NSs³.

S8. XPS spectra of WS2 and TiS2 NSs



Fig. S7 (a) XPS spectra of W 4f core level energy regions for WS_2 NSs prepared by ULI; (b) XPS spectra of Ti 2p core level energy regions for TiS₂ NSs prepared by ULI.

XPS spectra of W 4f core level peak regions in Fig. S7a can be deconvoluted into three groups of peaks with binding energy ranging from 40 eV to 30 eV: (1) The doublet peaks located at 32.1 eV and 34.3 eV can be assigned to W $4f_{7/2}$ and W $4f_{5/2}$ of 1T-WS₂, respectively; (2) The doublet peaks located at 33.2 eV and 35.3 eV originate from W $4f_{7/2}$ and W $4f_{5/2}$ of 2H-WS₂, respectively; (3) The peak around 37.7 eV belongs to W 5p, according to the reported literature⁴. The results show that W atoms in as-prepared WS₂ NSs have +4 oxidation state. Fig. S7b shows the XPS spectra of Ti 2p core level energy regions of TiS₂ NSs. The peaks near 458.0 eV and 463.8 eV can be assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively⁵.

(b) (a) WS, bulk TiS, bulk WS, nanosheets TiS, nanosheets \mathbf{E}^{1}_{2g} $\mathbf{A}_{1\mathbf{g}}$ A_{1g} E_{1g} Intensity (a.u.) Intensity (a.u.) 350 200 250 300 400 450 200 250 300 350 400 450 Raman shift (cm⁻¹) Raman shift (cm⁻¹)

S9. Raman spectra of WS2 and TiS2 NSs

Fig. S8 Raman spectra of (a) WS₂ NSs films and (b) TiS₂ NSs films prepared by ULI.

There are two distinct Raman scattering peaks (351.6 cm⁻¹ and 415.9 cm⁻¹) for WS₂ NSs prepared by ULI method (Fig. S8a), which belong to the in-plane E_{2g}^1 and out-of-plane A_{1g} modes, respectively. Compared with WS₂ powder, E_{2g}^1 vibration stiffens slightly, which indicates that the

as-prepared WS₂ NSs has small thickness⁶. The Raman peaks located at 331 cm⁻¹ and 229 cm⁻¹ of TiS₂ NSs can be ascribed to E_{1g} and A_{1g} vibrational modes, respectively (Fig. S8b)⁷. There is a bout 2 cm⁻¹ shift of E_{1g} peak compared with bulk TiS₂, suggesting a decrease of the layer numbers⁵.

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